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Description

The present invention relates to a method of synthesizing diamond under diamond-stable superhigh pressure and temperature by employing carbon sources, solvent metals for dissolving said carbon sources and seed crystals thereby growing diamond crystals.

Diamond is a material having the highest hardness and modulus of elasticity among the existing materials. Further, extremely pure diamond has such superior characteristics that it has the highest thermal conductivity and high transmittance of light in infrared regions. Thus, diamond is one of the precious resources that cannot be replaced by other materials.

There are generally two types of methods for synthesizing diamond. In one of such methods, carbon material is mixed or brought into contact with a solvent metal such as iron, cobalt or nickel to be subjected to diamond-stable superhigh pressure and temperature whereby the carbon is converted into diamond under the action of the solvent metal. According to such method, the solvent metal penetrates into the carbon material (generally prepared by graphite), whereby the carbon is caused to diffuse through the solvent metal which is in the form of a thin film, to generate diamond. The driving force for diamond generation in this method is the difference in solubility between graphite and diamond with respect to the solvent metal under a constant temperature. According to this method, diamond is spontaneously nucleated, and rapidly grows until it reaches a certain size. A considerable quantity of fine diamond powder has generally been synthesized by this method to be applied to, e.g., abrasives.

However, larger diamond crystals of high quality cannot be synthesized by the aforementioned method.

On the other hand, a method of synthesizing large diamond crystals of good quality is disclosed in US—A—3,297,407. Fig. 1 roughly illustrates a synthesizing vessel as employed in this method. Such prior art method is now described with reference to Fig. 1.

Diamond seed crystals 1 are located in upper and lower portions of the synthesizing vessel as shown in Fig. 1. A carbon source 2 is provided between the two diamond seed crystals 1, with solvent metal layers 3 arranged in the upper and lower sides of the carbon source 2. A cylindrical heater 4 is adapted to heat the synthesizing vessel.

The synthesizing vessel in the above structure is heated to the maximum temperature at its central portion in the axial, i.e., vertical direction, while the upper and lower end portions thereof are heated at relatively low temperatures.

Carbon dissolved in the solvent metal layers 3 under diamond-stable superhigh pressure and temperature is precipitated as diamond on the seed crystals 1, which are under relatively low temperatures. This method utilizes difference in solubility of carbon with respect to the solvent metal based on temperature difference, and is called as a temperature difference method. Such temperature difference method enables growth of diamond only from diamond seed crystals, while enabling control of diamond growth rate by maintaining the temperature difference at prescribed value. Therefore, large diamond in one carat size can be synthesized in the laboratory according to said method.

However, in the aforementioned temperature difference method, a superhigh pressure generator required for the synthesis process is extremely expensive while a considerable time is required for the synthesis process. Therefore, the cost for synthesizing diamond is greatly increased, and hence no large diamond has been produced in the industrial field in practice.

The technique of synthesizing diamond based on the aforementioned temperature difference method is further described in "Some Studies of Diamond Growth Rates" by R. H. Wentorf, Jr., the Journal of Physical Chemistry, Vol. 75, No. 12, 1971, pp. 1833—1837. Fig. 2 shows a synthesizing vessel employed in the prior art as disclosed in this literature. The difference between the synthesizing vessels as shown in Figs. 1 and 2 resides in that a partition wall is provided at the central portion in the axial, i.e., vertical direction of the vessel as shown in Fig. 2, and the both vessels are substantially identical to each other in other points. As also shown in Fig. 2, the synthesizing vessel is provided with vertically symmetrical temperature distribution such that the vessel is under a relatively high temperature at its axial center, with temperatures being lowered toward the upper and lower ends thereof.

According to an experiment made in practice in the synthesizing vessel as shown in Fig. 2, a large diamond crystal of good quality can be synthesized in the lower part of the vessel, whereas no good diamond crystal can be grown in the upper part thereof even if the temperature distribution and materials of components are prepared to be the same as those of the lower part. The reason for this is described in the aforementioned literature by Wentorf, Jr. (see pages 1834 to 1835), and considered to be based on the action of gravity. In other words, when the solvent metal is molten and carbon is dissolved in the solvent metal, the solvent metal is reduced in specific gravity. Such reduction in specific gravity follows increase in temperature. Under such circumstances, dissolution of the carbon in the solvent metal is caused in the upper end portion of the solvent metal in the lower part of the synthesizing vessel, while the temperature is raised higher in the said upper end. However, the result is contrary to this in the upper part of the synthesizing vessel. Thus, the specific gravity of the solvent metal is at the minimum in the lower end of the upper vessel part, whereby conversion is caused by the action of gravity. Consequently, the carbon is excessively supplied to the upper end on which the seed crystal is located, leading to impossibility in retaining the appropriate rate for growing good diamond crystals. Thus, according to the conventional

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method of synthesizing diamond based on the temperature difference, good diamond crystals can be synthesized only in the lower part of the synthesizing vessel as shown in Fig. 2. Therefore, the cost for synthesizing diamond is further increased in the conventional method utilizing the temperature difference method.

5 Another example of a method of synthesizing diamond on the basis of temperature difference is disclosed in JP-A-88289/1977, which points out other disadvantages of the conventional method of synthesizing diamond by the temperature difference method. The disadvantages pointed out in the prior art literature are that, in the conventional process of synthesizing diamond based on the temperature difference method, spontaneous nucleation takes place in portions other than seed crystals thereby to 10 reduce the yield of synthesized diamond crystals as grown on the seed crystals, that it is difficult to obtain diamond crystals of uniform quality and size, and that grown diamond crystals tend to be cracked. The JP-A-88289/1977 then discloses a method of preventing generation of diamond crystals in portions other than the seed crystals. This method comprises a step of placing a shielding layer for preventing nucleation between the solvent metal layer and the seed crystals, which shielding layer is prepared by a transition 15 metal such as cobalt (Co), iron (Fe) and manganese (Mn) applicable as a solvent to diamond or a carbide-generating element such as titanium (Ti), chromium (Cr) and tungsten (W).

However, according to experiments made by the inventors, it has been found that the method disclosed in JP-A-88289/1977 still has the following disadvantages: Although the transition metal such as Co, Fe and Mn can effectively be employed as the material for the shielding layer for preventing 20 nucleation when the solvent metal is prepared by a metal having low carbon solubility such as nickel (Ni) or Fe-Ni alloy, such shielding layer of the transition metal cannot effectively prevent nucleation when the solvent metal is prepared by that having high carbon solubility such as Fe, Co or an alloy mainly composed of these metals. Further, employment of the element which generates a carbide such as W and Cr leads to deterioration in quality of finally obtained diamond crystals, which is not preferable since fine crystals of 25 carbides such as W and Cr generated simultaneously with the diamond crystals tend to be trapped in the diamond crystals.

Accordingly, it is the object of the present invention to provide a diamond synthesizing method which can synthesize a number of large diamond crystals of high quality simultaneously from a plurality of seed crystals.

30 This object is achieved by a method of synthesizing diamond
1. A method of synthesizing diamond under diamond-stable superhigh pressure and temperature by employing carbon sources (12a, 12b), solvent metals (13a, 13b) for dissolving said carbon sources and seed crystals (11a, 11b) thereby growing diamond crystals, characterized by the steps of:
dividing a synthesizing vessel (10) into at least two synthesizing chambers (10a, 10b) by at least one 35 partition layer (16);
placing said solvent metals (13a, 13b) being different from each other in eutectic temperature with respect to carbon into said synthesizing chambers;
heating said synthesizing vessel (10) to produce temperature differences between the respective end portions of said solvent metals;

40 placing said carbon sources in contact with the highest temperature end portions of said solvent metals;
placing said seed crystals in the lowest temperature end portions of said solvent metals; and
growing diamond crystals in said solvent metals in said synthesizing chambers.

The diamond synthesizing method in accordance with the present invention can effectively prevent 45 nucleation in portions other than seed crystals thereby to obtain large diamond crystals of high quality.
Preferably the divided synthesizing chambers are arranged in a plurality of stages in the vertical direction in said synthesizing vessel,
at least one heat generator (14) is arranged in the outer peripheral portion of said synthesizing vessel for heating the same,

50 said synthesizing vessel being provided with a temperature gradient wherein the upper part along the axial direction of said synthesizing vessel is at a high temperature and the lower part at a low temperature, and

55 said plurality of solvent metals different in said eutectic temperature are placed in said synthesizing chambers so that a solvent metal having relatively higher eutectic temperature with respect to carbon is positioned in the synthesizing chamber in said upper part and a solvent metal having relatively lower eutectic temperature with respect to carbon is positioned in the synthesizing chamber in said lower part of said synthesizing vessel.

The temperature for synthesizing diamond in said synthesizing chambers are different from each other, the lower end of the solvent metal in the coolest synthesizing chamber being at a temperature in 60 excess of 1000°C, the pressure for synthesizing diamond being in excess of 40 kb.

According to the present invention having the aforementioned structure, large diamond crystals of high quality can simultaneously be produced at a low cost.

A method of synthesizing diamond wherein a plurality of said seed crystals are placed with respect to one solvent metal in each of said synthesizing chambers and a method of synthesizing diamond wherein 65 said plurality of seed crystals are placed in concentration in excess of $1/\text{cm}^2$ in effective regions capable of

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growing crystals effectively prevents nucleation in portions other than the seed crystals.

Preferred embodiments of the invention will be described with reference to the accompanying drawings, in which:

5 Fig. 1 is a cross sectional view showing an example of a diamond synthesizing vessel employed in a conventional diamond synthesizing method;

Fig. 2 is a schematic cross sectional view showing another example of a diamond synthesizing vessel employed in a conventional temperature difference method, in which a temperature gradient is also shown in the right-hand side of the synthesizing vessel;

10 Fig. 3 is a cross sectional view of a synthesizing vessel employed in the present invention, which also illustrates a temperature gradient within the synthesizing vessel in the right-hand side;

Fig. 4 is a diagram for illustrating the principle of the present invention, shown in which are pressure and temperature regions capable of synthesizing diamond;

15 Fig. 5 is a cross sectional view showing another example of a synthesizing vessel employed in the present invention;

Fig. 6 is a schematic cross sectional view for illustrating an example of a heat generator employed for carrying out the present invention;

Fig. 7 is a cross sectional view for illustrating another example of a heat generator employed in the present invention; and

20 Fig. 8 is a cross sectional view for illustrating another embodiment of the present invention, in which a plurality of seed crystals are placed in a single synthesizing chamber.

As shown in Fig. 3, a synthesizing vessel 10 is arranged inside a cylindrical heater 14. The synthesizing vessel 10 is divided by a partition layer 16 into a pair of synthesizing chambers 10a and 10b. The partition layer 16 is prepared by a material not reactive to a solvent metal, such as pyrophyllite or sodium chloride (NaCl).

25 Solvent metal layers 13a and 13b are located in the synthesizing chambers 10a and 10b. Carbon sources 12a and 12b are arranged to be in contact with the upper portions of the solvent metal layers 13a and 13b, while seed crystals 11a and 11b are placed to be in contact with the lower portions thereof. In the embodiment as shown in Fig. 3, the seed crystals 11a and 11b are so embedded in the partition layer 16 and a bottom wall 17 that only the upper surfaces thereof are exposed. Such synthesizing vessel 10 as shown in 30 Fig. 3 is disposed in a well-known superhigh pressure apparatus such as that disclosed in US-A-3,297,407.

The feature of the synthesizing vessel 10 as shown in Fig. 3 resides in that the carbon sources 12a and 12b, the solvent metal layers 13a and 13b and the seed crystals 11a and 11b are arranged in the same direction in both of the synthesizing chambers 10a and 10b. The temperature gradient along the axial direction of the entire synthesizing vessel 10, i.e., the vertical direction is as indicated in the right-hand side in Fig. 3. Namely, the temperature in the upper synthesizing chamber 10a is kept relatively higher than that in the lower synthesizing chamber 10b.

According to the present invention, a plurality of diamond crystals can be simultaneously grown utilizing the synthesizing vessel 10 as shown in Fig. 3. Description is now made on such process.

40 When the synthesizing vessel 10 as shown in Fig. 3 is adapted to synthesize diamond, temperature differences ΔT_1 and ΔT_2 are caused between the respective upper and lower end portions of the solvent metal layers 13a and 13b in the respective stages, i.e., the respective synthesizing chambers 10a and 10b. Such temperature differences are caused in the solvent metal layers 13a and 13b between portions in contact with the carbon sources 12a and 12b and those in contact with the seed crystals 11a and 11b.

45 On the other hand, Fig. 4 is an illustration showing a diamond-to-graphite equilibrium line and changes in eutectic temperatures of the employed solvent metals with respect to carbon. When, for example, the eutectic temperature of the solvent metal as employed is AA' in Fig. 4, diamond can be synthesized in the pressure-temperature region as defined by AA'K. Therefore, assuming that temperatures of the upper and lower ends of the solvent metal layer 13a in the upper synthesizing chamber 10a in Fig. 3 are respectively indicated by O and P and those of the upper and lower ends of the solvent metal layer 13b in the lower synthesizing chamber 10b are respectively indicated by Q and R, the values O, P, Q and R being as shown in Fig. 4, diamond crystals can be synthesized in both of the synthesizing chambers 13a and 13b by employing a metal whose eutectic temperature is indicated by AA' in Fig. 4 for forming the catalyst metal layer 13a in the upper synthesizing chamber 10a, while employing that whose eutectic temperature is indicated by BB' (see Fig. 4) for forming the solvent metal layer 13b in the lower chamber 10b.

50 The solvent metal having the eutectic temperature BB' may be considered applicable to both of the upper and lower stages, i.e., the synthesizing chambers 10a and 10b. However, although synthesis of diamond itself can be performed in both of the synthesizing chambers 10a and 10b, such application of the solvent metal is not preferable in view of synthesizing diamond crystals of high quality. This is because the 55 quality of diamond crystals depends on synthesizing temperature conditions and hence considerable volume of impurities are inevitably trapped in the crystals when the diamond is synthesized under a temperature remarkably higher than the eutectic temperature of the solvent metal. Consequently, it is difficult to synthesize diamond crystals of high quality.

60 It is impossible to synthesize diamond in the lower stage, i.e., the lower synthesizing chamber 10b if the solvent metal having the eutectic temperature AA' is also employed in the synthesizing chamber 10b.

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As hereinabove described, when the synthesizing vessel 10 as shown in Fig. 3 is employed, the solvent metal layers 13a and 13b different from each other in eutectic temperature with respect to carbon are located in the synthesizing chambers 10a and 10b respectively, whereby large diamond crystals of high quality can be grown simultaneously on the two seed crystals 11a and 11b.

5 Fig. 5 is a cross sectional view showing another example of a diamond synthesizing vessel applicable to the present invention. A synthesizing vessel 20 as shown in Fig. 5 is entirely provided with a temperature gradient in a constant direction. In other words, the temperature is made to be lowered from the top stage toward the bottom of the synthesizing vessel 20 as shown in Fig. 5. Such temperature gradient can be attained by providing, on the upper portion of a cylindrical heater 24, a disc-shaped heater 28 which is
10 adapted to close the cylindrical heater 24 and a heater 29 having a small section arranged in contact with the disc-shaped heater 28.

15 The synthesizing vessel 20 is divided in the axial, i.e., vertical direction into four stages by partition layers 26a, 26b and 26c, thereby to define divided synthesizing chambers 20a, 20b, 20c and 20d. The bottom portion of the lowermost synthesizing chamber 20d is defined by a bottom wall 27 of the synthesizing vessel 20.

20 Located within the respective stages, i.e., the respective synthesizing chambers 20a, 20b, 20c and 20d are carbon sources 22a to 22d, solvent metal layers 23a to 23d and seed crystals 21a to 21d successively from above. The seed crystals 21a to 21d are respectively placed in plural in the respective synthesizing chambers 20a to 20d.

25 In the synthesizing vessel 20 as shown in Fig. 5, diamond crystals can be synthesized simultaneously in the four synthesizing chambers 20a to 20d by the temperature difference method, by appropriately setting thickness values of the partition layers 26a to 26c and/or the solvent metal layers 23a to 23c and employing four types of solvent metals whose eutectic temperatures are different from each other as indicated by AA', BB', CC' and DD' in Fig. 4.

30 25 As hereinabove described, the present invention employs such a synthesizing vessel 10 or 20 as shown in Fig. 3 or 5, namely, the respective synthesizing chambers are so constructed that diamond crystals are grown upwardly from seed crystals, whereby a number of large diamond crystals of high quality can be simultaneously obtained. In other words, although only one stage of synthesizing vessel can be utilized in the conventional method based on the temperature difference method, a large-sized synthesizing vessel can be effectively utilized according to the present invention by applying such structure as shown in Figs. 4 and 5, thereby to enable efficient mass production of diamond crystals, leading to remarkable reduction in synthesizing cost.

35 The solvent metals employed in the present invention may be prepared by well-known solvent metals generally applied to diamond synthesis, e.g., metals such as iron, cobalt, nickel, manganese and chrome, or alloys thereof, or alloys thereof and other metals. It is preferable to employ alloys including prescribed volume of carbon as the solvent metals, in order to prevent dissolution of the seed crystals as described in JP—A—69211/1981. Further, blue semiconducting diamond can be synthesized by adding boron (B) as described in the aforementioned literature by Wentorf, Jr. Similarly, transparent diamond can also be synthesized by adding nitrogen getter such as aluminum (Al), titanium (Ti) and zirconium (Zr).

40 The solvent metals different in eutectic temperature with respect to carbon may be selected from the aforementioned metals or alloys. For example, in the Ni-Mn alloy system, the eutectic temperature with respect to carbon under a pressure of 52 kb is continuously changed from 1400°C to 1100°C as the content of manganese (Mn) is increased from 0 to about 54 percent by weight. Therefore, solvent metals of appropriate alloy composition may be selected in compliance with the temperature gradient of the 45 synthesizing vessel. It is to be noted that, in practice, the lower limit temperature for synthesizing diamond is higher by several ten degrees from the eutectic temperatures of the solvent metals and carbon under a specific pressure.

45 The carbon source as employed in the present invention is preferably prepared by graphite or mixture of graphite and fine diamond powder.

50 The seed crystals are prepared by fine diamond particles. The partition layers for dividing the synthesizing vessel into a plurality of stages are in contact with the solvent metals, and hence required to be selected from materials not reactive to the same, e.g., oxides such as aluminum oxide (Al_2O_3), zirconium oxide (ZrO_2) and magnesium oxide (MgO), halides such as sodium chloride ($NaCl$) and potassium chloride (KCl), minerals such as pyrophyllite and talc, and various carbides and nitrides. The partition layers are also utilized as seed beds for the seed crystals, as shown in Figs. 3 and 5. The vessel for containing the carbon sources, the solvent metal layers and the seed crystals is formed by a pressure medium such as pyrophyllite, $NaCl$ and BN.

55 The temperature differences of the solvent metal layers required for carrying out the present invention are within the range of 10°C to 150°C, preferably within the range of 20°C to 100°C. The diamond growth rate is reduced when the temperature differences are insufficient, while no good crystals can be obtained if the temperature differences are excessive.

60 An apparatus for synthesizing diamond according to the method of the present invention is approximately implemented by a belt or girdle type apparatus, and also by other superhigh pressure generator device such as a cubic anvil device and a pistoncylinder type device. Pressure-temperature 65 conditions for synthesizing diamond according to the present invention vary with the solvent metals as

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employed. In order to synthesize diamond of good quality, the cooler portions of the solvent metal layers in which the diamond crystals are grown must be heated at temperatures exceeding 1000°C, and the pressure required is over 40 kb.

Various methods are considered applicable for providing the synthesizing vessel with the temperature gradient in a constant direction. Applicable to the present invention are a method of varying the sectional shape of a heater 34 as shown in Fig. 6 thereby to heat the upper portion of the synthesizing vessel at a higher temperature, a method of dividing a cylindrical heat generator into a plurality of layers 44a, 44b and 44c as shown in Fig. 7 thereby to vary the materials of the heater layers in order to lower specific resistances of the layers successively from the top stage and a combination of these methods.

10 Description is now made on Examples of the present invention.

Example 1

A synthesizing vessel in the structure as shown in Fig. 5 was employed in this Example. The solvent metal layer in each stage was 25 mm in diameter and 6 mm in thickness, and the uppermost stage was prepared by Ni, the second stage by 50Fe-50Ni alloy, the third stage by 64Fe-31Ni-5Co alloy, and the fourth stage by 40Fe-40Ni-20Mn alloy. The respective carbon source was formed by an embossed disc plate prepared by diamond powder and graphite powder mixed in the ratio of 2:1 by weight. Synthetic diamond crystals of about 0.7 mm in diameter were employed as the seed crystals, and embedded in partition layers of NaCl to be in contact with the bottom surfaces of the respective solvent metal layers. Seven seed crystals were applied to each stage. Pyrophyllite was applied as a pressure medium to the outer peripheral portion of the graphite heat generator, while the partition layers were prepared by NaCl. A girdle-type superhigh pressure press was employed. An electrical current was passed through the heater after giving pressure. As a result, the synthesizing vessel was heated under a pressure of 55 kb, so that the bottom surface of the Ni layer in the top stage is heated at a temperature of about 1450°C. The bottom surface temperature of the 40Fe-40Ni-20Mn alloy layer in the fourth stage was about 1220°C at this time. These conditions were retained for 60 hours. As the result, diamond crystals of about 0.5 carat size were grown from the seed crystals in the respective stages, and the total yield was 35 carats.

Example 2

30 The synthesizing vessel was in the same structure as Example 1, and the solvent metal layers were prepared by Ni, Ni-15Mn alloy, Ni-30Mn alloy and Ni-45Mn alloy successively from the top stage. The seed crystals were embedded in partition layers of NaCl. The pressure-temperature conditions were identical to those in Example 1, and retained for 60 hours. In the first synthesizing vessel employing Ni as the solvent metal, no spontaneous nucleation was observed. On the other hand, in the second to fourth synthesizing 35 vessels, there were only a few spontaneous nucleations in portions other than the seed crystals. However, the quality of the diamond crystals obtained in the second to fourth stages and grown on the seed crystals was the same as that obtained in the first vessel. In the synthesizing vessel employing the Ni-Mn solvent metals divided into two to four stages, small diamond particles were grown by spontaneous nucleation in addition to diamond crystals of 0.3 to 0.4 carat size grown from the seed crystals, and the total yield was 25 carats.

Example 3

45 The synthesizing vessel was formed in the structure as shown in Fig. 3. The respective solvent metal layer was 12 mm in diameter and 5 mm in thickness, and the upper stage layer was prepared by 50Fe-50Ni alloy, the lower stage by 64Fe-31Ni-5Co alloy. The carbon sources were formed by embossed members of mixed powder of diamond and graphite similarly to Example 1. The seed crystals were prepared by synthetic diamond particles of about 0.7 mm in diameter, three in each stage. The synthesizing vessel was heated under a pressure of 52 kb so that the upper surface temperature of the upper solvent metal layer was 1400°C. It was estimated that the lower surface temperature thereof was about 1370°C, and the upper 50 and lower surface temperatures of the lower solvent metal layer were 1350°C and 1280°C respectively at this time. These conditions were retained for 30 hours, and as the result, three diamond crystals of about 0.1 carat size were grown in the upper stage while three diamond crystals of about 0.3 carat size were grown in the lower stage.

55 It is understood from the aforementioned Examples 1 to 3 that large diamond crystals of high quality can be obtained according to the method of the present invention. The inventors have further found that larger diamond crystals of better quality can be obtained by placing seed crystals in the respective synthesizing chambers in concentration in excess of a certain extent. In other words, when diamond is synthesized on the basis of the conventional temperature difference method as hereinabove described, a considerable amount of nucleation takes place in portions other than the seed crystals, thereby to lower the 60 yield and quality of the diamond crystals grown on the seed crystals. JP-A-88289/1977 discloses the structure of providing the shielding layer for preventing nucleation between the solvent metal layer and the seed crystals, in order to overcome the aforementioned problem. However, it has been difficult to obtain large diamond crystals of high quality by this method, as hereinabove described. The inventors have found that large diamond crystals of high quality can be obtained without providing any shielding layer for preventing deteriorous nucleation by locating a plurality of seed crystals 61 in a synthesizing chamber 50 to

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be in contact with a solvent metal layer 62 as schematically illustrated in Fig. 8, in concentration of one or more to 1 cm². Numeral 63 in Fig. 8 indicates a carbon source. The concentration of the seed crystals may be in excess of 1/cm², and preferably within the range of 50/cm² in practice, in order to obtain larger diamond crystals. According to the method of the present invention, there is no restriction in the types of

5 the solvent metals to be employed, in contrast to the method as disclosed in JP—A—88289/1977. On the other hand, the characteristics of diamond single crystals greatly depend on the characteristics of the solvent metals employed for synthesizing the diamond crystals. Therefore, according to the present invention, the solvent metals can be freely selected in response to the characteristics to be obtained.

As hereinabove described, spontaneous nucleation in portions other than the seed crystals can be 10 effectively prevented by locating a plurality of seed crystals in concentration in excess of 1/1 cm² in a single synthesizing chamber for the following considerable reason: Under conditions for growing crystals of good quality, the number of nuclei as formed is in the range of zero to several tens with respect to the area of 1 cm² of regions capable of growing crystals, i.e., the base area of the solvent metal layer in most cases. It has been found that such nucleation is facilitated in the initial stage of crystal growth, and formation of 15 nuclei is remarkably reduced with progress of crystal growth. In consideration of this point, it is supposed that, when seed crystals are placed at least in a number equal to or exceeding the number of crystals upon completion of nucleation, the number of nuclei as formed will not exceed the said number. This supposition was confirmed by the following experiment made by the inventors:

An abrasive grain of synthetic diamond of about 0.5 mm was employed as a seed crystal and 20 embedded in a NaCl disc plate of 20 mm in diameter, which was applied to a base plate for crystal growth. A disc plate of 49Fe-51Ni alloy was placed thereon as the solvent metal, on which a member of mixed powder of high purity graphite and diamond was placed as a carbon source. These members were contained with a pressure medium and an energizing heater in a superhigh pressure vessel, to be subjected to two experiments for retaining the same under pressure of 52 to 54 kb and temperature of 1340 to 1400°C 25 for 50 hours. Grown in the first experiment were five in total of crystals of 0.2 to 0.4 carat size based on spontaneous nucleation in addition to a diamond crystal of 0.6 carat size grown on the seed crystal. One of the diamond crystals grown on the basis of the spontaneous nucleation was in contact with the diamond crystal grown on the seed crystals, and the both diamond crystals were cracked at the contact portions upon releasing of the pressure. In the second experiment, six diamond crystals of 0.15 to 0.3 carat size were 30 grown in addition to a diamond crystal of 0.7 carat size grown on the seed crystal.

Additionally, two experiments were respectively made on seed crystals in numbers of 0, 1, 4, 10 and 30 at regular intervals, under the same conditions as the aforementioned two experiments. Results are as shown in Table 1.

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Table 1
 Results of Experiments made on Different Numbers of Seed Crystals
 (average value of two experiments)

Number of Seed Crystals	Concentration of Seed Crystals (/cm ²)	Number of Nuclei as formed	Total Yield (carat)	Yield of Crystal grown on Seeds	Weight per Crystal (carat)
0	0	10.5	2.3	0	0.22
1	0.32	7.5	3.0	0.9	0.35
4	1.27	2.0	4.6	3.0	0.77
10	3.18	0.5	6.2	6.1	0.58
30	9.55	0	6.7	6.7	0.22

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It has been confirmed from the results as shown in Table 1 that the number of nuclei as formed besides seed crystals is reduced as the number of seed crystals is increased. Thus, it is understood that spontaneous nucleation can substantially completely be prevented by securing a sufficient number of seed crystals.

5 The aforementioned effective concentration of 1/cm² has been found by the inventors on the basis of the foregoing supposition and experiments. Definite Examples are now described.

Example 4

An experiment was made by the same method and conditions as the experiments made in relation to 10 the results in Table 1. The solvent metal was prepared by pure cobalt, and ten seed crystals were placed at regular intervals. These seed crystals were embedded in a NaCl disc plate. As the result, ten crystals of 0.23 to 0.44 carat/number were grown all on the seed crystals. The total yield was 3.9 carats. No nucleation was observed in portions other than the seed crystals.

15 Example 5

An experiment was made with a solvent metal prepared by 70Fe-30Co and 60 seed crystals in the same method and conditions as Example 4. As the result, 58 crystals of 0.048 to 0.096 carat/number were grown all on the seed crystals. Two of the seed crystals were dissolved. The total yield of the crystals as obtained was 4.7 carats. No nucleation was observed in portions other than the seed crystals, similarly to Example 4.

20 Example 6

An experiment was made with a solvent metal prepared powder metallurgically by 63.5Fe-32Co-4.5C in the same method and conditions as Example 5. As the result, 60 crystals of 0.63 to 0.11 carat/number were grown all on the seed crystals. No nucleation and no dissolving of seed crystals were observed in portions 25 other than the seed crystals. The total yield of crystals as obtained was 5.3 carats.

Example 7

An experiment was made with using 120 seed crystals and retaining a reaction vessel for 60 hours in the same method as Example 6. Other conditions were the same as Example 6. As the result, 120 crystals of 30 0.25 to 0.41 carat/number were grown all on the seed crystals. No nucleation was observed in portions other than the seed crystals. The total yield of the crystals as obtained was 3.4 carats.

Claims

35 1. A method of synthesizing diamond under diamond-stable superhigh pressure and temperature by employing carbon sources (12a, 12b), solvent metals (13a, 13b) for dissolving said carbon sources and seed crystals (11a, 11b) thereby growing diamond crystals, characterized by the steps of:
dividing a synthesizing vessel (10) into at least two synthesizing chambers (10a, 10b) by at least one partition layer (16);
40 placing said solvent metals (13a, 13b) being different from each other in eutectic temperature with respect to carbon into said synthesizing chambers;
heating said synthesizing vessel (10) to produce temperature differences between the respective end portions of said solvent metals;
placing said carbon sources in contact with the highest temperature end portions of said solvent 45 metals;
placing said seed crystals in contact with the lowest temperature end portions of said solvent metals;
and
growing diamond crystals in said solvent metals in said synthesizing chambers.
2. A method of synthesizing diamond in accordance with claim 1, wherein
50 said synthesizing chambers are arranged in a plurality of stages in the vertical direction in said synthesizing vessel,
at least one heat generator (14) is arranged in the outer peripheral portion of said synthesizing vessel for heating the same,
said synthesizing vessel being provided with a temperature gradient wherein the upper part along the 55 axial direction of said synthesizing vessel is at a high temperature and the lower part at a low temperature, and
said plurality of solvent metals different in said eutectic temperature are placed in said synthesizing chambers so that a solvent metal having relatively higher eutectic temperature with respect to carbon is positioned in the synthesizing chamber in said upper part and a solvent metal having relatively lower eutectic temperature with respect to carbon is positioned in the synthesizing chamber in said lower part of 60 said synthesizing vessel.
3. A method of synthesizing diamond in accordance with claim 2, wherein temperatures for synthesizing diamond in said synthesizing chambers are different from each other, the lower end of the solvent metal in the coolest synthesizing chamber being at a temperature in excess of 1000°C, the pressure for synthesizing diamond being in excess of 40 kb.

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4. A method of synthesizing diamond in accordance with claim 1 or 2, wherein a plurality of said seed crystals are placed with respect to one solvent metal in each of said synthesizing chambers.

5. A method of synthesizing diamond in accordance with claim 4, wherein said plurality of seed crystals are placed in concentration in excess of 1/cm² in effective regions capable of growing crystals.

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Patentansprüche

1. Verfahren zur Diamantsynthese unter diamantstabilem superhohem Druck und superhoher Temperatur mit Hilfe von Kohlequellen (12a, 12b), Lösungsmittelmetallen (13a, 13b) zur Lösung der Kohlequellen und Kristallkeimen (11a, 11b), so daß Diamantkristalle wachsen, dadurch gekennzeichnet, daß ein Synthesegefäß (10) mit Hilfe wenigstens einer Trennschicht (16) in wenigstens zwei Synthesekammern (10a, 10b) unterteilt wird,

daß die Lösungsmittelmetalle (13a, 13b), die bei eutektischer Temperatur in Bezug auf Kohle voneinander verschieden sind, in die Synthesekammern eingebracht werden,

daß das Synthesegefäß (10) erhitzt wird, um Temperaturunterschiede zwischen den jeweiligen Enden der Lösungsmittelmetallen herstellen,

daß die Kohlequellen in Kontakt mit denjenigen Enden der Lösungsmittelmetalle gebracht werden, die die höchste Temperatur aufweisen,

daß die Kristallkeime in Kontakt mit denjenigen Enden der Lösungsmittelmetalle gebracht werden, die die niedrigste Temperatur aufweisen, und

daß Diamantkristalle in den Lösungsmittelmetallen in den Synthesekammern wachsen.

2. Verfahren zur Diamantsynthese nach Anspruch 1, wobei

die Synthesekammern in einer Vielzahl von Stufen in vertikaler Richtung in dem Synthesegefäß angeordnet sind,

wenigstens ein Wärmeerzeuger (14) in dem äußeren peripheren Teil des Synthesegefäßes zur Erwärmung desselben angeordnet ist,

das Synthesegefäß ein Temperaturgefälle aufweist, bei dem der obere Teil in axialer Richtung des Synthesegefäßes eine hohe Temperatur und der untere Teil eine niedrige Temperatur aufweist, und

die Vielzahl von Lösungsmittelmetallen, die bei eutektischer Temperatur voneinander verschieden sind, in die Synthesekammern eingebracht werden, so daß ein Lösungsmittelmetal, das eine in Bezug auf Kohle relativ höhere eutektische Temperatur aufweist, in der Synthesekammer in dem oberen Teil angeordnet ist und ein Lösungsmittelmetal, das eine in Bezug auf Kohle relativ niedrigere Temperatur aufweist, in der Synthesekammer in dem unteren Teil des Synthesegefäßes angeordnet ist.

3. Verfahren zur Diamantsynthese nach Anspruch 2, wobei die Temperaturen für die Diamantsynthese in den Synthesekammern voneinander verschieden sind, das untere Ende des Lösungsmittelmetalls in der kühlssten Synthesekammer eine Temperatur von über 1000°C aufweist, und der Druck für die Diamantsynthese über 40 kb beträgt.

4. Verfahren zur Diamantsynthese nach Anspruch 1 oder 2, wobei eine Vielzahl von Kristallkeimen in Bezug auf ein Lösungsmittelmetal in jede der Synthesekammern eingebracht werden.

40 5. Verfahren zur Diamantsynthese nach Anspruch 4, wobei die Vielzahl von Kristallkeimen in einer Konzentration von mehr als 1/cm² in Wirkungsbereich plaziert werden, in denen Kristalle wachsen können.

Revendications

45 1. Procédé de synthèse de diamant sous une pression et à une température ultrahautes assurant la stabilité du diamant, en utilisant des sources de carbone (12a, 12b), des métaux-solvents (13a, 13b) pour dissoudre ces sources de carbone et des cristaux de germination (11a, 11b), de façon à provoquer une croissance de cristaux de diamant, caractérisé par les étapes consistant à:

subdiviser une cuve à synthèse (10) en au moins deux chambres à synthèse (10a, 10b), par au moins une couche de séparation (16);

introduire, dans lesdits chambres à synthèse, lesdits métaux-solvents (13a, 13b) présentant une température eutectique différente l'une de l'autre vis-à-vis du carbone;

chauffer ladite cuve à synthèse (10), afin d'engendrer des différences de température entre les régions extrêmes respectives desdits métaux-solvents;

mettre lesdites sources de carbone en contact avec les régions extrêmes à température maximale desdits métaux-solvents;

mettre lesdits cristaux de germination en contact avec les régions extrêmes à température minimale desdits métaux-solvents; et

développer, dans lesdites chambres à synthèse, des cristaux de diamant dans lesdits, métaux-solvents.

2. Procédé de synthèse de diamant selon la revendication 1, dans lequel

lesdites chambres à synthèse sont agencées en de multiples étages dans le sens vertical de ladite cuve à synthèse,

au moins un générateur de chaleur (14) est installé dans la zone périphérique externe de ladite cuve à synthèse, pour chauffer cette dernière,

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ladite cuve à synthèse étant munie d'un gradient thermique tel qu'il règne une température élevée dans la partie supérieure, le long de la direction axiale de ladite cuve à synthèse, et une basse température dans la partie inférieure et

lesdits multiples métaux-solvants dont la température eutectique diffère sont placés, dans lesdites 5 chambres à synthèse, de façon telle qu'un métal-solvant ayant une température eutectique relativement plus élevée, par rapport au carbone, soit placé dans la chambre à synthèse située dans ladite partie supérieure, et qu'un métal-solvant ayant une température eutectique relativement plus basse, par rapport au carbone, soit placé dans la chambre à synthèse située dans ladite partie inférieure de ladite cuve à synthèse.

10 3. Procédé de synthèse de diamant selon la revendication 2, dans lequel des températures de synthèse de diamant sont mutuellement différentes dans lesdites chambres à synthèse, l'extrémité inférieure du métal-solvant situé dans la chambre à synthèse la plus fraîche étant soumise à une température excédant 1000°C, la pression de synthèse de diamant excédant 40 kb.

15 4. Procédé de synthèse de diamant selon la revendication 1 ou 2, dans lequel de multiples cristaux de germination précités sont agencés par rapport à un seul métal-solvant dans chacune desdites chambres à synthèse.

5. Procédé de synthèse de diamant selon la revendication 4, dans lequel lesdits multiples cristaux de germination sont placés, en une concentration excédant $1/\text{cm}^2$, dans des zones actives aptes à développer des cristaux.

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FIG.1

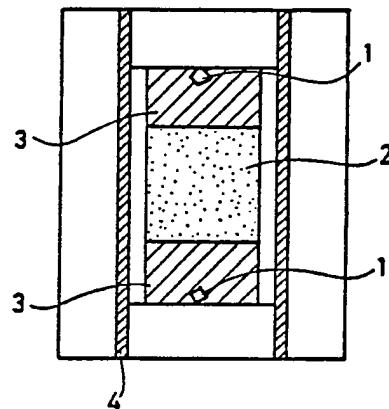


FIG. 2

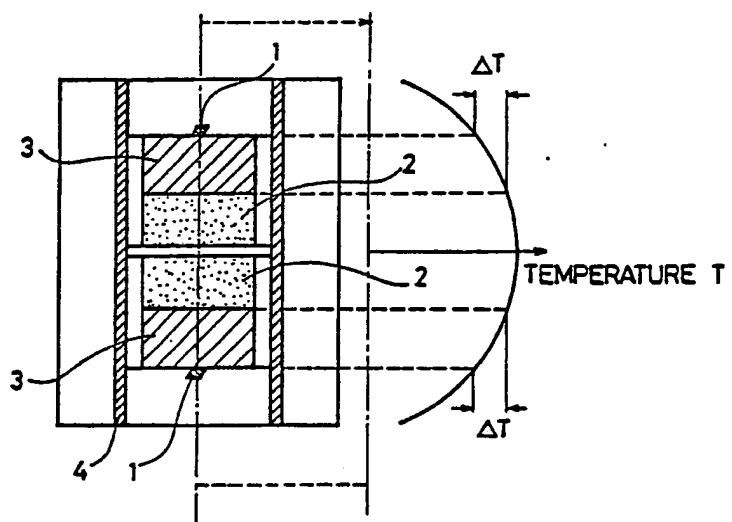
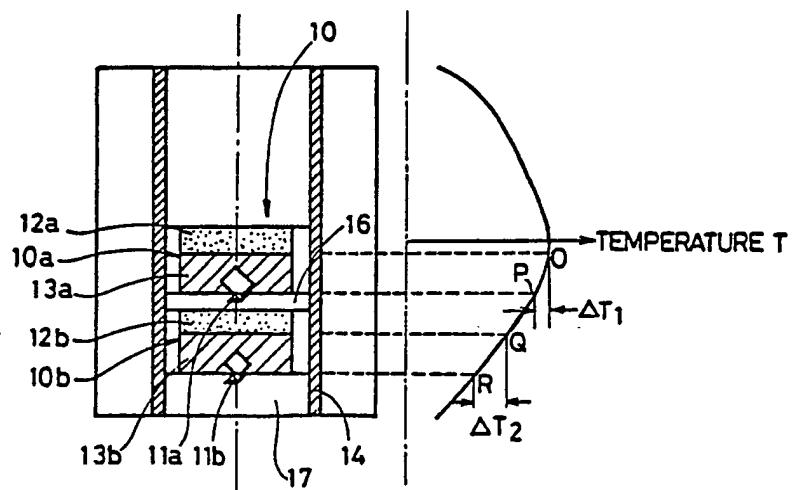


FIG. 3



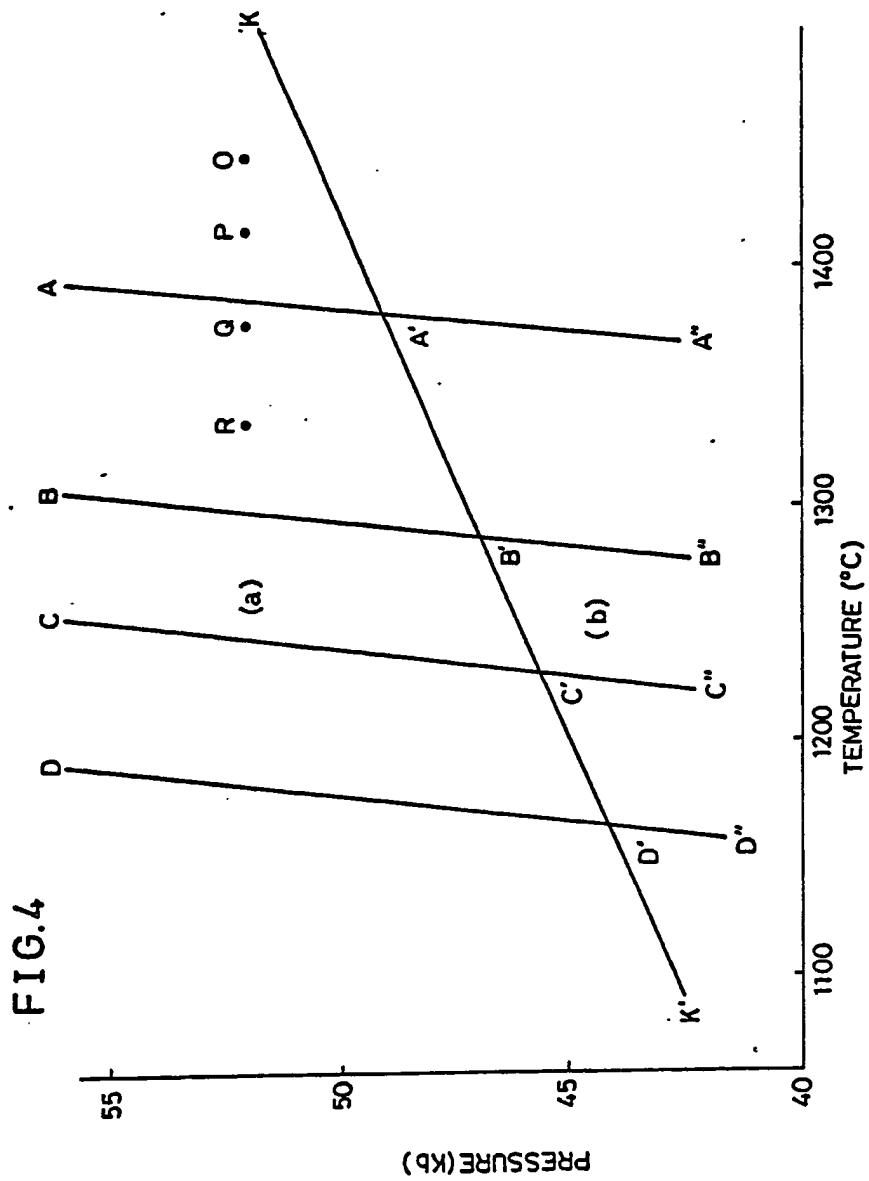


FIG.5

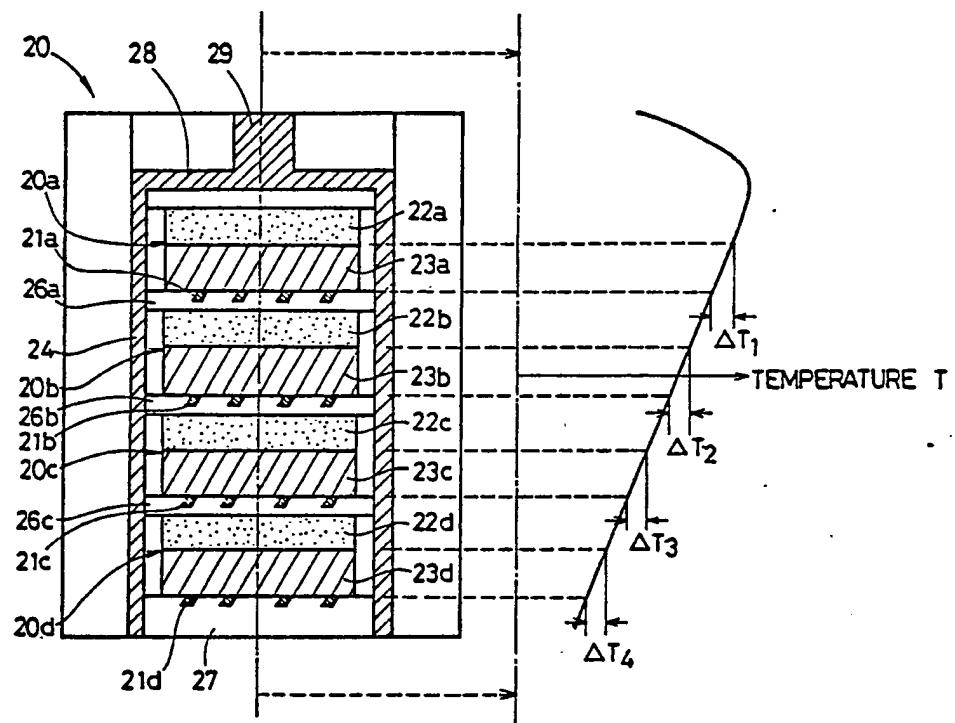


FIG.6

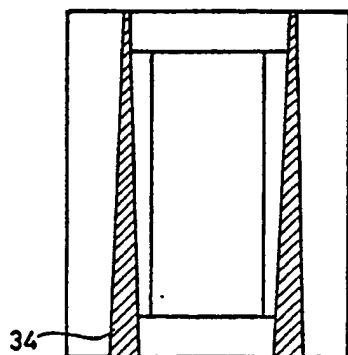


FIG.7

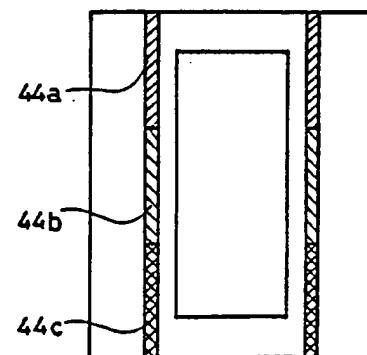


FIG. 8

